

PETCOKE & METHANOL—2 (Conclusion)

How blending petcoke methanol into gasoline might work

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This two-part series analyzes the economics of producing 50,000 b/d of methanol for gasoline blending from petroleum coke (petcoke) and examines some aspects of using methanol-gasoline blends for motor fuel. Corn-based ethanol-gasoline (10 vol % blend) serves as a reference case.

Part 1 (OGJ, June 6, 2011, p. 114) presented the production flow scheme we have developed and discusses utilities requirements and basic process parameters.

This concluding article presents some of the issues in using methanol blended with gasoline to fuel cars and light trucks, as perhaps an M-10 blend. It includes a capital cost estimate and introduction to some peripheral issues such as CO₂ capture for enhanced oil recovery (EOR).

Fig. 1 from Part 1 has been reproduced here for ease of reference.

Methanol to gasoline

The potential conversion of methanol to gasoline (MTG) deserves a few words. The first commercial MTG unit was licensed by Mobil Oil in New Zealand in 1985.¹

The anticipated yield from 50,000 b/d of methanol could be 20,500 b/d gasoline (rvp 9 psia, before ethanol blending; 0.73 sp gr; RON 92, benzene 0.3 vol %). And it produces about 5,500 b/d of C₃-C₄ LPG.

On this basis, it is difficult to see any rationale in converting methanol to gasoline if the option of methanol-gasoline blending is available. According to information from the US Environmental Protection Agency, methanol blending into gasoline is not banned in the US.

Given the investment in MTG facilities and the shrinkage in energy content (8-9%), and energy consumed by the MTG plant, the cost of the MTG gasoline would be significantly above the cost of energy in the methanol.

In this context, it is worth adding that conversion of syngas to hydrocarbon liquids by Fischer-Tropsch synthesis is

technically proven and produces high-quality diesel.² At the same time the coproduced naphtha is very paraffinic, with an octane value of perhaps 35 to 40 and is essentially nonreformable for octane elevation. Further, no steam cracker for ethylene production in Alberta is adaptable for liquid naphtha feed.

CO₂ capture; EOR

The total carbon input to gasification is about 6,555 tonnes/day (tpd) of carbon. In addition, the boilers are fed with of a 50/50 mix of petcoke and subbituminous coal. About 640 tpd of this mixture meets the process energy demands, when no power is exported.

The total carbon entering the complex, therefore, is 7,177 tpd. The methanol product contains 2,400 tpd of carbon leaving.

The remaining carbon is therefore 4,777 tpd. The captured CO₂, which is compressed by a single multi-stage centrifugal compressor of about 42,000 kw to sequestration or EOR, is 11,700 tpd. This represents 67% carbon capture.

If power is exported, the CO₂ capture drops to about 60%, because that captured is within the methanol synthesis, whereas the CO₂ released is in the boiler stacks.

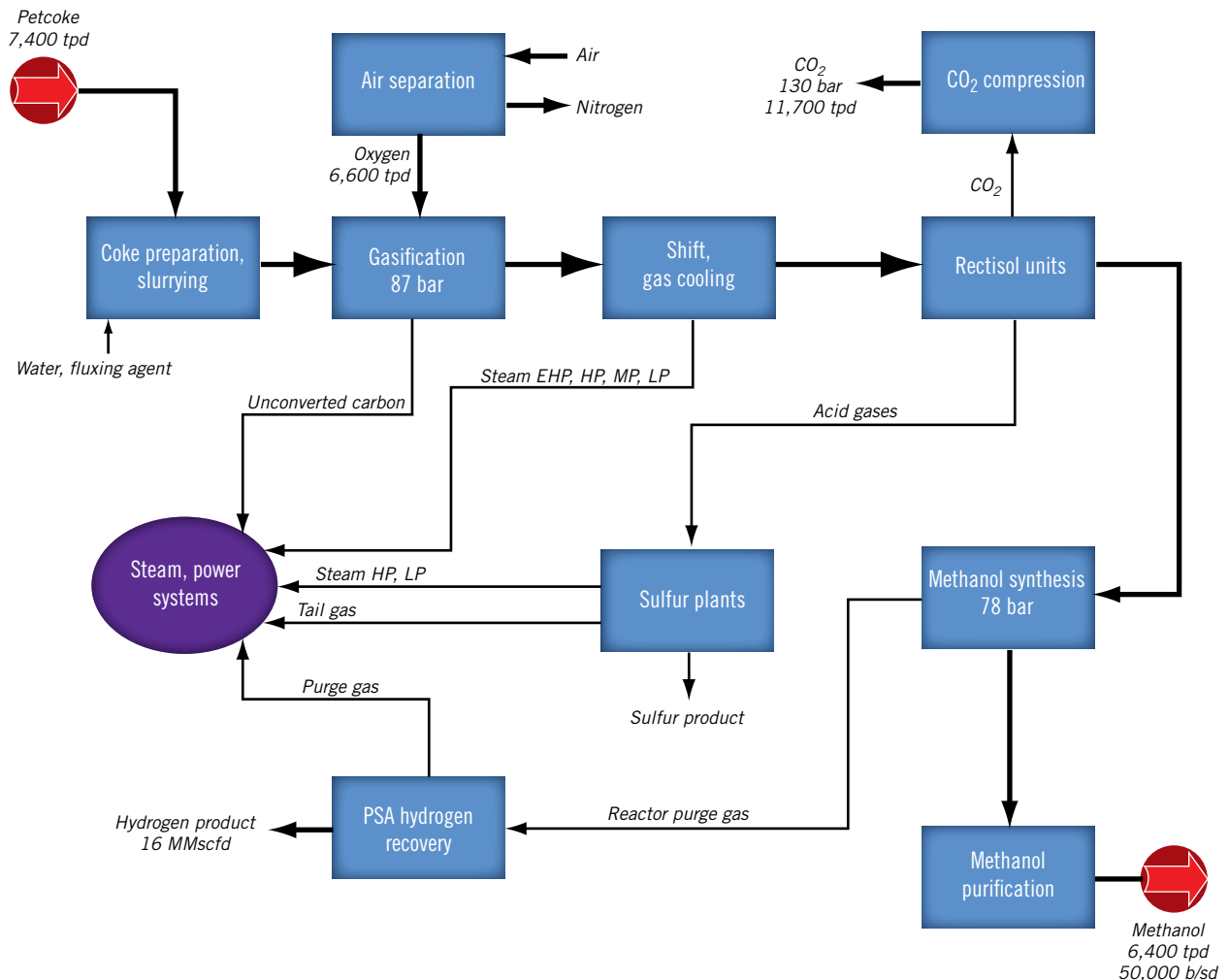
As a side note: If part of the fuel for the boilers was from biomass then some of the stack CO₂ is not counted as a release because it originated from the atmosphere and is being “returned” not “released.”

In summary, about 0.93 to 1.25 tonnes of CO₂ is released pre ton of methanol (about 258 to 346 lb/bbl). This CO₂ release per barrel is about on par with the CO₂ release from all sources in producing corn-based ethanol, which is calculated by EPA methodology that uses 22% “renewability” to be at least 320 lb/bbl.

About 8,800 tpd of CO₂ is released in internal combustion engines while consuming the methanol product as gasoline blend. The total CO₂ release from “mine to wheel” is therefore about 650 lb/bbl. The CO₂ release “mine to wheel” by combustion of ethanol, using the equivalent methanol energy content of 34% lower than ethanol, is about 640 lb/bbl (adjusted to net combustion energy).

The potential for using CO₂ for EOR in Alberta could become a major positive economic contributor. Based on information published by Enhance Energy and others related to

PETCOKE TO METHANOL



a prospective CO₂ trunk line project in Alberta,³ the average performance of EOR is 0.32 tons of CO₂/bbl of oil recovered. The ultimate potential crude oil recovery in Alberta is about 1 billion bbl. On this basis, the 11,700 tpd of CO₂ could be used to recover some 36,000 b/d of crude oil. At this point, however, the disposition of the CO₂ and the economic consequences are unclear.

The safety issues and concerns of long-term underground CO₂ sequestration are captured in the following from the Jan. 13, 2011, Calgary Herald: “[Alberta] Premier Ed Stelmach vowed Thursday the province will not proceed with storing carbon emissions underground without research showing the practice is safe.”

To the best of the authors’ knowledge, the issue of CO₂ capture in proposed US “clean coal” projects for power generation is still an open issue.⁴ It is generally accepted that the estimated capital investment for these projects is far larger

than anticipated and uses at least 20% of the gross power production (and thus close to 30% of additional coal consumed) to drive the capture apparatus and associated peripheral units.

Blends: methanol vs. ethanol

All past analyses have evaluated methanol-gasoline blend toxicity and safety issues as pure methanol compared with regular reformulated gasoline. No similar analysis is known in which an ethanol-gasoline blend was used as a reference case. Since 10 vol % ethanol blending will be mandated by the US EPA, it would be appropriate to use the ethanol blend as a reference case.

The following methanol toxicity, environmental, and safety issues have been raised in the past:

1. Accidental methanol ingestion by humans.
2. Vapor displacement of methanol during filling of auto-

PRICING: ETHANOL VS. GASOLINE, POTENTIAL GASOLINE BLENDSTOCK

Table 1

	Octane RON	LHV, btu/US gal	Oxygen, wt %	Price, US\$/gal, Oct 2010 Before tax and distribution
Reformulated gasoline	92	116,000	—	2.13
Methyl tertiary butyl ether	110	101,000	18	2.44
n-Butane	91	95,000	—	1.56
Ethanol	113	76,400	35	1.52
Methanol	129	57,000	50	0.88

mobile gasoline tanks.

3. Accidental methanol spillage from trucks and rail cars during transportation to market distribution.

4. Biological degradation issues.

5. Leakage of methanol-gasoline blend to groundwater.

6. Elevated Reid vapor pressure due to the presence of methanol.

7. Absorption of water vapor from the atmosphere by methanol-gasoline blends.

In order to analyze this issue objectively, we compared typical gasoline compositions in North America with unpublished data for rvp. Typical North American motor gasolines are blended with 2-10 vol % n-butane, depending on seasonal adjustments for rvp considerations. Canadian gasoline (especially in winter) can contain at least 8 vol % n-butane. Under the California Air Resource Board, the state's gasoline may have only negligible, if any, butane blending.

In addition, the US EPA will mandate 10 vol % ethanol blending, for the following stated reasons:

1. Use oxygenated compound to reduce emission of hydrocarbons, CO, and NOx.

2. In order to mitigate climate change, ethanol is considered by the EPA as 22% renewable and is thus in line with EPA's stated policy of minimizing global warming.

3. Reduce US reliance on imported crude oil and consequential impact on trade balance.

For all these issues, we examined gasoline as blended with 3 vol % n-butane and 10 vol % ethanol as a reference or control case. Methanol blending in the range of 7-10 vol % was used to examine the rvp safety and toxicity issues.

Note that a recent study in Italy examined a variety of potential gasoline "oxygenates" for possible carcinogenic properties (the study included both ethanol and methanol),¹¹ Some ethers were found to be possibly carcinogenic; neither of the alcohols were.

Methanol, if ingested by mouth at more than 10 cc, is dangerously toxic and can cause blindness.⁴ If methanol is blended with gasoline at the proposed 7-10 vol % range, however, the blend is far more toxic than methanol alone. Ingestion by mouth of 10 cc of gasoline, or gasoline-ethanol blend or gasoline-methanol blend could cause immediate harm; the toxicity of the methanol-gasoline is no greater (or less) than the other gasolines.

Therefore, pure methanol toxicity is inconsequential in

the application discussed here because it will not be encountered by the public.

Vapor displacement

Most modern vehicles in the US are equipped with a fuel vapor-recovery system, and most fueling stations in the US have hoses that incorporate a vapor-recovery suction hose. These are

called Stages 1 and 2 vapor recovery.

Therefore, vapor displacement has been minimized in recent years and is getting smaller as older cars leave the road. Currently, filling station vapor recovery in Canada is not widely practiced.

We consider an ultraconservative scenario in which 15 gal of air and fuel vapor are displaced during fueling (that is, no vapor-recovery system is present or working). Methanol and gasoline vapors, or ethanol and gasoline vapor in the control case, are released. Further, to be as conservative as possible, we assume that a single adult inhales the entire displaced vapors.

If we use 7-psi total hydrocarbon partial pressure including 1.7-psi methanol partial pressure, then the total methanol released during displacement is about 1.5 gal of vapor. At atmospheric pressure, this is about 8 g of methanol. We must assume the adult concerned somehow survives the "suffocating gas" exclusion of inhaled oxygen.

The "incidental" inhalation of about 4 times as much gasoline as methanol will be far more injurious. Analysis of risks related to potential exposure to skin would result in similar conclusions. We conclude that the presence of methanol in gasoline blends does not increase toxicity concerns.

Spillage; biological degradation

Chemical-grade methanol in tonnage quantities is being moved daily for industrial and petrochemical consumers. Well-established environmental and safety procedures promulgated by US and Canadian governmental agencies are in force for this. Moving methanol for distribution to gasoline blending does not represent a new challenge.

Further, ethanol as a gasoline blend is denatured before transportation (by adding noxious or toxic denaturants). Neither alcohol is inherently "safe" for bulk transportation. Because both alcohols are highly miscible and soluble in water, there is no differential risk of spillage contamination of ground or surface waters. A small concentration of methanol in water is not toxic.

Methanol, unlike MTBE, is highly biodegradable. A hypothetical study related to the Exxon Valdez crude oil spillage accident in March 1989 indicated that had the oil tanker that collided with the reef been loaded with methanol, instead of crude oil, the effects of the accident would have disappeared within 3-5 days.⁵

Methanol released into the environment has an accepted half-life of 1 day, compared with the half-life of Benzene (or Toluene) in gasoline of more than 2 years.

This fuzzy issue has been discussed over at least the last 15 years. Recent EPA and OSHA regulations about buried tanks help to minimize the possibility of leakage to groundwater. Unlike MTBE, methanol is highly biodegradable and diluted methanol-water mixture is essentially odorless.

It is possible that the solubility of benzene, a known toxic constituent of gasoline, in groundwater would increase with the presence of methanol.

However, two points need to be considered:

1. The benzene content in US gasoline was recently reduced by the EPA to about 0.5-0.6 vol %

2. The solubility of benzene in a methanol-water mixture is not substantially different from its solubility in an ethanol-water mixture. Therefore, the mandated ethanol blending in our reference case invalidates concerns about the “benzene solubility” issue for methanol in water.

Rvp issues

We analyzed the rvp for methanol blended (7% added methanol) with the gasolines under consideration. The calculated rvp is about 1.1 to 1.5 psi greater than the reference 10 vol % ethanol-gasoline blend. Given that in most gasoline pools some lower cost n-butane is blended, adjusting the butane content could easily mitigate this issue. However, the economic benefit of adding inexpensive methanol outweighs this effect.

In the Edmonton area and in much of the US even during summer, methanol blend rvp is not an issue, due to low ambient temperatures.

Note that ethanol also raises the rvp of gasoline by more than 1.0 psi. For this reason, the EPA granted a waiver (or series of waivers) to allow a 1.0-psi increase in finished gasoline rvp as part of the mandate for E-10 fuel. This waiver could reasonably be applied to M-10 blends—if only because there is no nonpolitical reason not to.

Combustion of pure methanol, like hydrogen fuel, yields flames that are colorless (invisible) in daylight. This presents a fire-fighting safety hazard. Nevertheless combustion of 10% or even 30% gasoline-methanol blend has full color flames (and smoke).

The water absorption issues of methanol-gasoline blend

INSTALLED CAPITAL COSTS

Table 2
\$ million

1. Petroleum coke storage, preparation, and coke wet grinding: two 50% trains including coke slurry storage tanks	85
2. Gasification: four quench gasifiers, four soot scrubbers, two carbon recovery and ash-removal systems	260
3. Air separation and oxygen compression: two 50% trains	350
4. Shift and gas cooling including precooling: two 50% trains	80
5. Rectisol acid-gas removal: two 50% trains	315
6. Single Rectisol refrigeration train	50
7. Sulfur-recovery unit: two 100% units	95
8. Methanol synthesis: two 50% trains, 100% recycle compressor	140
9. PSA and PSA purge-gas compression	10
10. Methanol purification: two 50% trains	50
11. CO ₂ compression: one 100% train	65
12. Steam and power generation: three 55% steam boilers	160
13. One 100% med. press. steam superheater and one 100-Mw power generator	75
14. One electric power generators, 100 Mw	65
15. Condensers	15
16. DNOx tail end scrubbing: single train	35
17. Boiler feedwater pumps	12
18. Emergency diesel generator: 5 Mw	10
19. Auxiliary boilers systems: three 50%	40
20. Cooling water	55
21. Interconnecting piping	70
22. Waste-water treating: single 100%	15
23. Methanol storage and intermediate storages: 2 x 250,000 bbl	45
24. Site preparation: 200 acres	10
25. CO ₂ pipeline to injection	50
26. Miscellaneous off sites and general infrastructure	110
Subtotal	\$2,277
Adjustment to Edmonton location +16%	2,641
Owner cost +6%	158
Total	\$2,799

are not substantially different from those for an ethanol-gasoline blend, in terms of absorption of atmospheric moisture. Further, for seasonal yard machines such as gasoline-powered lawn mowers, there is a widely accepted practice (recommended by many manufacturers of such machines) to add a trace of methanol, ethanol, or isopropanol to the fuel tank before winter storage.

This is to avoid fuel-tank condensed water separation; the alcohol causes small quantities of condensed water to “redissolve” into the gasoline phase. There are widely available retail products, many consisting almost entirely of methanol, for such “gasoline drying” and freeze protection.

Potential production for gasoline

Total US gasoline consumption, according to weekly reports from the US Energy Information Administration, is on the order of 9 million b/d and a portion of it is imported as finished gasoline. Total North American gasoline market is about 10 million b/d.

Total coking capacity in the US is on the order of 2.5 million b/d, equivalent to a total US coke production of about 120,000 tpd. A large fraction of this fuel-grade coke could be available for methanol production. This would suggest that perhaps 600,000 b/d of methanol, or about 6.5% of US gasoline, could potentially be produced as discussed from Petcoke.

In Alberta the potential petcoke production, from bitumen upgrading, is about 50,000 tpd. This means Alberta

could, potentially, produce about 300,000 b/d of methanol.

Before the currently mandated ethanol blending into gasoline, MTBE was the common oxygen carrier blended in gasoline. Due to reported incidents, especially in California, of accidental leak to groundwater, this blending was banned in the US.

As a replacement to MTBE, ethanol was introduced to the US gasoline pool. The reasons behind the mandated ethanol blending policy were encapsulated in the US Energy Security Act of 2007:

1. Ethanol, like MTBE and methanol, provides the “oxygenate” constituents in gasoline, thereby reducing auto exhaust emission of NOx and hydrocarbons.

2. Ethanol, like MTBE and methanol, enhances octane and reduces the T-50 (mid boiling point) of gasoline.

3. Ethanol, being 22% renewable according to EPA methodology, will result in lower emission of “greenhouse gases.”

4. Ethanol will reduce crude oil imports, which should have a positive effect on national security and help balance the national budget.

5. It was recognized that ethanol blending would increase the rvp of gasoline (as does methanol). Therefore, the EPA has introduced several waivers for ethanol-gasoline blending which mitigate these rvp issues.

Table 1 presents recent pricing of ethanol compared with gasoline and potential gasoline blend stocks:

The October 2010, \$1.52/gal pricing of ethanol is after a \$0.45/gal federal subsidy, and as shown the volumetric energy content of ethanol is 33.5% lower than average gasoline blends. The gasoline price is based on October 2010 US Gulf Coast at \$80/bbl WTI crude oil, which is a common benchmark.

The price of methanol of \$0.88/gal reflects the results of this study, using conservative economic assumptions. The current market price of methanol (spot, May 2011) is around \$1.04/gal on the US Gulf Coast.

A comment by Secretary of Energy Chu encapsulates some sense of the direction of US government philosophy on ethanol-gasoline blending: “Ethanol is not an ideal transportation fuel. The future of transportation fuels shouldn’t involve ethanol” (press release, US Department of Energy, Nov. 29, 2010).

To the best of our knowledge, all the attempts so far to produce cellulosic (second-generation) ethanol have yielded no more favorable economic results compared with the first-generation ethanol. But such technology is a laudable direction to proceed because it would avoid the current situation, in which, in effect, food is being burned in vehicle engines.

Renewability

The petcoke feed to the complex proposed in this series of articles has already been produced. In many respects it is a waste byproduct (or has very low value). As such, it is not part of the finite fossil hydrocarbon reserves of our planet.

Therefore we consider that this proposition, and the motor fuel it produces, is outside of the normal “renewable vs. non-renewable” considerations.

At the moment methanol-gasoline blend is commercially used in several provinces in China, where much of the methanol is produced by coal-gasification processing. It should be noted that gasification of coal and gasification of petroleum coke are very similar, although for the most part gasification of petroleum coke results in better economics.

Roland Yap of the Methanol Institute of Singapore has said methanol fuel blends are used in at least 15 Chinese provinces: Below are four provinces where, with provincial government support, there appears to be the most activity in using methanol fuel blends:

- Shanxi Province: M5-M15 and M85-M100.
- Shaanxi Province: M15 only.
- Zhejiang Province: M15, M25, and M30.
- Guizhou Province: M15 only.

Other methanol use

Pure methanol has been extensively used as racing fuel, often because the high octane rating allows higher compression ratios and higher specific power outputs. Some dragsters, midgets, and sprint cars, monster trucks and other ultra-high performance motor sports use M-100 fuel to this day. (A “Top Fuel” dragster uses a forced-induction nitromethane-methanol fuel blend to achieve phenomenal, if short-lived, specific power output of the order of 1,000+ BHP/l. engine displacement.)

Another interesting note: Indy Car fuel, until recently, was mandated as M-100 because of “safety concerns.” A car crash and fire in 1964 on the Indianapolis 500 race when the fuel was gasoline gave an intense cloud of black smoke. This obscured the view of the track for following drivers and resulted in a deadly multi-car pile-up in which two drivers died.

The Indy Car authorities changed the rules to mandate M-100 fuel because it has clear flames and no smoke, and therefore a car fire would not obscure the view of the track.

Vehicle performance

North American spark-ignition vehicles are all currently designed for gasoline fuel with 10% ethanol. This fuel results in a slightly lower mileage than “straight” gasoline would give because of the lower volumetric energy content of ethanol compared with gasoline hydrocarbon species. Methanol has an even lower volumetric energy content, and therefore vehicles fueled with a M-10 or M-5/E-5 blends would suffer a small fuel mileage penalty.

The penalty for M-10 compared with E-10 (on a purely volumetric energy content basis), however, is only about 1.5%, which is an imperceptible change.

Note that E-10 has a vehicle-mileage penalty, on the same basis, of almost 3.5% compared with unblended “straight”

gasoline, and yet this much larger penalty went essentially unnoticed by the motoring public.

By contrast, M-10 has a higher octane rating because 100% methanol has an RON value of 129 compared with ethanol of 113. This enhanced octane value would allow gasoline producers slightly to reduce high-value reformate, isomerate, and alkylate content of finished M-10 gasoline to achieve the same octane value as current E-10 fuel.

These effects are all small or negligible in their overall effect upon the gasoline pool. Vehicles fueled with either E-10 or M-10 will exhibit essentially unchanged performance, mileage and driveability. If the M-10 fuel has a slightly higher effective octane value, the modern ECM-equipped engines will find a slightly higher resistance to pre-detonation, and adjust the engine parameters (particularly ignition timing) to perform slightly more efficiently.

Needed modifications

Ford, GM, and others sell flex-fuel vehicles in the US designed to use a variety of ethanol-containing fuels up to perhaps E-85. The engine control modules on these cars can use the exhaust oxygen sensors to modify engine control parameters slightly to adapt to the fueled ethanol blend. In addition, the various fuel system components are specified to be fully resistant to corrosion or swelling caused by ethanol.

The 15+ year trial in California, from 1980 to 1995, of using M-100 to fuel a fleet of state-owned vehicles, found some early corrosion and blockage/plugging issues.⁷ These were attributed, after extensive investigation, to be due to:

- Corrosion of aluminum and aluminum alloys within the fuel systems: methanol can corrode aluminum.
- Dissolving some polymers or polymer additives from fuel hoses and gaskets.

It was determined that changing

component alloys or plating the metal parts totally avoided corrosion. Modern polymers, for hoses, gaskets, and O-rings, are virtually fully resistant to methanol attack. These simple and inexpensive upgrades avoid potential plugging or blockages in M-100 fueled vehicles. For blends such as M-10 or our suggested M-5/E-5 blends, it is not clear that any modifications are required beyond the current “E-10 fuel” configuration.

For fully fuel-flexible vehicles, which can adapt to 100% gasoline or any combination up to E-100 (or

M-100) the vehicle needs an addition of a fuel analyzer of some type. This tells the engine electronic control module (ECM) what the characteristics of the fuel in the tank are, for a feed-forward adaptation of the engine parameters. Such an analyzer, which could add perhaps \$500 to the cost of a car, is totally unnecessary for “modest” blends such as M-5/E-5 or M-10 etc.

The overall conclusion is that modern US spark-ignition cars and light trucks, which are mandated to be designed for E-10 fuel, require no modi-

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fications whatsoever to use M-5/E-5 or M-10 blends of gasoline.

Another comment worthy of note: When oxygenates were first added to gasoline (in Los Angeles, to reduce smog, for example), the reduction in harmful tailpipe emissions was measurable and large. Most cars and light trucks had carburetors, and relatively “dirty” or inefficient engines. (The very first fuel injection on a mass-produced US car was not until a 1976 model.)

Since then there has been a major revolution in engine design and configuration. Engines now use fuel injection, either “direct” or throttle-body-inlet port types. The fuel injection, ignition timing, sometimes valve timing or lift are now controlled by very sophisticated electronic (computer) systems. These have measurements of exhaust oxygen content, combustion chamber predetonation or “pinging,” coolant and ambient air temperatures, air pressure and (often) the user profiles or habits of the driver. Exhaust gas is recirculated to the inlets; spark plugs are now precious-metal tipped; and myriad other major improvements.

All these measures are aimed squarely at fuel economy and efficiency but have the serendipitous effect of greatly reducing “nasty” tailpipe emissions. A modern car with these features is much “cleaner” even if fueled with straight (non-reformulated) gasoline. Their tailpipe emissions are orders of magnitude cleaner than a 1980s car with “oxygenates” in its fuel.

The rationale to add oxygenates to gasoline for cleaner emission, therefore, has been largely, if not wholly, supplanted.

Infrastructure modification

Both methanol and ethanol are hygroscopic, in that they can and will absorb atmospheric moisture. Because of this, and to reduce VOC emissions, vehicle fueling facilities in the USA are required to have “Stage II” vapor-recovery systems in place. The effect of this measure is to have the fuel storage and fueling apparatus at effectively positive pressure. This excludes ingress of atmospheric air.

The blending of alcohol with refinery-type gasoline components to produce finished gasoline is done at the source refinery or more often at major loading points. This system can remain unchanged for M-10 blends. The components within the blending, loading, and distribution systems are currently fully compatible with ethanol. It is unlikely that any changes to accommodate methanol will be required, or if needed will be very minor.

Capital cost estimate

This capital cost estimate is based on published information and discrete private sources and includes prospective license fees. The basis is the US Gulf Coast, January 2011. The investment in the Edmonton area is assumed to increase by 16% over USGC costs due to higher construction costs and climate,

material transportation, and local infrastructure issues

Table 2 presents the installed capital costs. The cost of startup, about 3.5%, is taken as an operating cost.

During the preparation of the material, we realized that issues of “financial engineering,” such as depreciation, rate of return, and other economic factors, are indeterminate for this concept. As such, we avoided preparing a detailed economic analysis.

Postscript: It should be noted that all our thinking was based on October 2010, when WTI was at around \$80/bbl. As this manuscript was going to press (May 2011), the price of WTI was hovering around \$100/bbl. Therefore, the economic incentive for methanol-gasoline blending via gasification of petcoke has markedly increased. **OGJ**

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